

Preparation and characteristic analysis of rice husk high boiling solvent lignin

CHEN Yun-ping^{1,2}, CHENG Xian-su^{1,2,*}

¹College of Material Science and Engineering, Fuzhou University, Fuzhou 350002, P. R. China;

²Department of Chemistry and Chemical Engineering, Minjiang University, Fuzhou 350108, P. R. China.

Abstract: Rice husk high boiling solvent lignin (RHL) was prepared by high boiling solvent method, and its characteristics was analyzed by using chemical composition analysis, infrared spectroscopy, and ¹H-NMR and ¹³C-NMR spectroscopy. The optimum prepared condition was that the rice husk with 70%–90% aqueous solution of 1, 4-butanediol was mixed with autoclave, under a certain weight ratio of solid raw material and solvent, heated to 200–220°C for 1.0–3.0 h, then water-insoluble RHL was separated from the liquor reaction mixture by water precipitation. Results suggested that the lower digestion temperature and concentration of 1,4-butanediol were both unfavorable for extracting lignin. Chemical weight-average molecular weight of RHL was 1939 g·mol⁻¹, and the residual polysaccharide content was 5.12%. The ¹H-NMR spectra of RHL showed the relative intensity ratio, aliphatic over aromatic methoxyl groups, situated at 3.5–3.8 and 3.8–4.0 ppm, respectively. The results from ¹³C-NMR spectra showed that β-O-4 bond and β-5 carbon–carbon linkage were the major linkages between RHL units. The C₉-formula of RHL was calculated by the experiment data.

Keywords: high boiling solvent method; rice husk lignin; C₉-formula

Introduction

Every year about one hundred million tons rice husk is produced in the world (Real et al. 1996), of which about thirty million tons come from China. Rice husk consists of some useful substance, such as lignin (the content about 25%), cellulose (about 40%), semi-cellulose (about 20%) and some ash (about 15%) (Jiang 2001). Nowadays, rice husk is often used as a source of fuel, or burnt directly to acquire the ash as fertilizer in China. Combustion of rice husk can not bring high value, but pollute environment by gas. High boiling solvent method can be used to separate the lignin from rice husk to increase the worth of rice husk (Chen et al. 2003; Cheng et al. 2004).

Lignin has the potential application as polymer-based products for different industries such as lignin-phenol formaldehyde resin,

lignin-isocyanate polyurethane adhesives, and foam insulation, etc. It is an amorphous aromatic network polymer made of the phenyl-propane units by carbon-carbon bonds and ether linkages, in which β-aryl ether linkage (48% in spruce and 60% in birch lignin) is the most dominant (Glasser et al. 1983; Nada et al. 1994). High boiling solvent (HBS) lignin is prepared by the high boiling organosolv, such as 1, 4-butanediol or ethylene glycol. This method was firstly introduced by Kajimoto et al. (2000) and used to analyze the structures of softwood and hardwood HBS lignin (Kajimoto et al. 2000; Widodo et al. 2000). However, the herbaceous plant was not mentioned in his paper. In the present study, we use this method to prepare the rice husk high boiling solvent lignin (RHL), which keeps up the original chemical activity perfectly. The potential application of RHL will be expanded, especially in material science and technology. For example, modified lignin resin by reaction with aldehyde can improve the property of NBR rubber, which the percentage of breaking elongation increased from 270 to 540. But the percentage of breaking elongation was 330% only when modified lignin sulfonate was added (Xu et al. 2004).

Chemical analysis as well as NMR and infrared spectroscopy was used to analyze the structure of RHL, and also to give information about the actual chemical group altered, removed and/or added to lignin during the pulping or reaction process (Nada et al. 1998). In the current work, the structural, physical and chemical characteristics of RHL were investigated by chemical analysis, infrared and NMR spectroscopy.

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Biography: CHEN Yumping (1975-), male, Assistant professor of Minjiang University, Fuzhou 350108, P.R. China

*Corresponding author, E-mail: chengxiansu@fzu.edu.cn

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Materials and methods

Preparation of RHL

Rice husk was from local products of Fujian Province; 1,4-butanediol (content > 99%) was imported from Mitsubishi Corporation in Japan; Catalyst was prepared by our group; Heating medium was oil (BP 300°C), obtained from Zhongyan Chemical Corporation in Jilin Province.

JF-Type Stainless Steel Autoclave (Working Pressure 1.5 MPa; Volume 10 L) made by Qingtian Electric Instrument Plant in Zhejiang Province and KSW-5-13 Temperature Controller made by Tianjin Scientific Instruments Corporation were used in preparation of RHL.

The samples of RHL were prepared by the following process. We put 1000-g rice husk into a 10-L stainless autoclave and added 70%–90% aqueous solution of 1,4-butanediol and small amount of acid catalyst to the autoclave, then heated to 200–220°C and kept this temperature for 60–180 min. Rice husk was easily pulped by the digestion. After digestion, the reaction mixture was cooled to 100°C. RHL solution was acquired by filtering. RHL solution was cooled to room temperature, and then three times volume of water was added to the RHL solution, stirring for 15 min. The precipitated lignin was collected by centrifugation and free-dried, and finally the RHL was obtained.

Chemical analysis

Methoxyl group analysis was performed by the Zeisel procedure. Elemental analysis was conducted by using Heraeus CHN-O-RAPID analyzer. Molecular weight was determined by using Waters-515 gel permeation chromatography. Tetrahydrofuran was used as flow solvent at 35°C.

Infrared spectroscopy

An infrared spectrum of RHL was obtained by using PE-2000 IR spectrometer. The sample was measured on KBr discs.

NMR spectroscopy

The ¹³C-NMR spectrum was recorded on BRUKER DRX-400 spectrometer. RHL sample was dissolved in DMSO-d₆ and placed in a 5-mm diameter tubes. The spectrum was recorded at the room temperature. The quantitative analysis and comparisons of signal intensities were used with the following parameters: 90° pulse angle, 3 s pulse delay, 16 K data points and number of scans 12000. The ¹H-NMR spectra of the RHL in CDCl₃ was obtained using the same spectrometer and operating at the room temperature.

Results and discussion

Results of L9 (3⁴) orthogonal experiment

The yield of rice husk lignin was chosen as the target. The reaction temperature, concentration of 1,4-butanediol, ratio of solid

materials with liquid, and the reaction time were selected as investigating factors to engage in L9 (3⁴) orthogonal experiments. The results of orthogonal experiments were listed in Table 1.

Table 1. L9 (3⁴) orthogonal experiment

Order of experiment	Reaction temperature/°C	Concentration of HBS %	The ratio of solid to liquid	Reaction time/min.	Lignin yield %
1	200	70	1:5	60	15.08
2	200	80	1:6	120	23.84
3	200	90	1:7	180	17.47
4	210	70	1:6	180	16.45
5	210	80	1:7	60	22.12
6	210	90	1:5	120	22.02
7	220	70	1:7	120	15.42
8	220	80	1:5	180	21.98
9	220	90	1:6	60	23.12
Average1	18.80	15.65	19.69	20.11	
Average2	20.20	22.65	21.12	20.43	
Average3	20.17	20.87	18.34	18.63	
Deviation between	1.40	7.00	2.78	1.80	
Averages					
Best combination	A ₂	B ₂	C ₂	D ₂	

The yield of RHL was over 22% under suitable digestion conditions (Table 1), which approaches the content of rice husk lignin theoretically. Some polysaccharide with lower molecular weight were condensed with lignin in recycling recovery solvent, which kept the fixed concentration of polysaccharide in the solvent and did not affect the yields of RHL.

The concentration of HBS had a great influence upon the yield of lignin. When the concentration of 1,4-butanediol was higher or lower, the yield of lignin became lower. Lower concentration of HBS was unfavorable for extracting lignin, because of reducing the solubility of lignin. On the one hand, some residue was acquired as materials for active carbon. On the other hand, a little water could promote the osmosis of solvent to enter the cell of rice husk. The optimum concentration of 1,4-butanediol for RHL preparation was 80% according to the orthogonal experiments. The second important factor affecting the digestion reaction was the ratio of solid to liquid. A higher ratio was directly influenced by the temperature-control. When the ratio of 1,4-butanediol was higher, the lignin concentration became lower. Lower ratio of solid to liquid can not immerge rice husk to solvent, which decreased the yield of lignin.

Through analyzing the deviation between average values, it was found that the influence of the temperature and reaction time on yields of the products were smaller in the selected experiment scopes. It also suggested that selecting a lower temperature could save the cost. When other conditions were the same, prolonging the reaction time might cause the degradation of lignin and make its yield lower. The best combination for higher yield of lignin was A₂B₂C₂D₂ according to the analysis of the deviation between average values of orthogonal experiments.

Chemical analysis

RHL was brown power separated by freeze-dry process. It could not be solved in water but alkali and phenol. The total polysaccharide content of HBS lignin was 5.12% according to Table 2, which was lower than that of the lignin sulfonate. It was favorable to manufacture the ramification of RHL (Cheng et al. 2004). Weight-average molecular weight of RHL was 1939 g·mol⁻¹ (Table 3). The poly dispersity was very near 1.0, indicating the very uniform separation. The element and the OCH₃ contents could establish the C₉ formula by calculation, all showed in the Table 4.

Table 2. Saccharide and ash content of rice husk lignin (RHL) and lignin sulfonate

Material	RHL	Lignin sulfonate
Saccharide content %	5.12	11.75
Ash content %	1.50	21.20

Table 3. Molecular weight of rice husk lignin (RHL)

Material	Mn*	Mw	Mz	d
RHL	1582	1939	3946	1.225

* Mn, number-average molecular weight; Mw, weight-average molecular weight; Mz, Z-average molecular weight; d = Mw/Mn

Table 4. Elementary composition of rice husk lignin (RHL)

Material	C(%)	H(%)	O(%)	N(%)	OCH ₃ (%)	C ₉ -formula
RHL	65.48	6.34	26.27	0.58	14.55	C ₉ H _{8.82} O _{2.12} (OCH ₃) _{0.85}

Infrared spectroscopy

IR spectra of RHL were shown in Fig. 1. Spectra of RHL showed a strong absorbance centered at about 1700 cm⁻¹, assigned to C=O in unconjugated ketones, carbonyls, and ester groups (Faix 1991). Some special absorption bands of lignin were observed in IR spectrum of RHL. The absorption bands in 1603 cm⁻¹ and

1515 cm⁻¹ were aromatic skeletal vibrations; a weak absorbance at 1665–1670 cm⁻¹ were C=O stretching conjugation to the aromatic rings; 1424 cm⁻¹ were C-H deformations of methyl and methylene. Moreover, syringyl and condensed guaiacyl absorptions were clearly seen at about 1329 cm⁻¹. The presence of a small shoulder at about 1219 cm⁻¹ was C-O stretching of syringyl. The bands at 1120 cm⁻¹ were assigned to C-O and C-C stretching vibrations, those at 1039 and 834 cm⁻¹ to aromatic C-H deformations (Vazquez et al. 1975; Scholze et al. 2001). Spectra of RHL showed a weak absorbance at 2300 cm⁻¹, assigned to C=C bond.

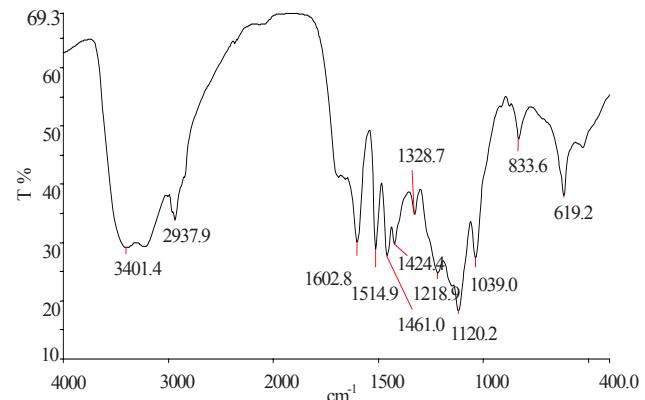


Fig. 1 infrared spectra of rice husk lignin (RHL)

¹H-NMR analysis

¹H-NMR spectra had been frequently used in lignin structural studies (Lundquist et al. 1986; Chen et al. 2002). Those spectra of the RHL were shown in Fig. 2. In addition to classical spectrum of hydroxyl–guaiacyl–syringyl lignin, the most characteristic feature was the relative intensity ratio, aliphatic over aromatic methoxyl groups, situated at 3.5–3.8 and 3.8–4.0 ppm, respectively. The ¹H NMR chemical shift of RHL was shown in the Table 5.

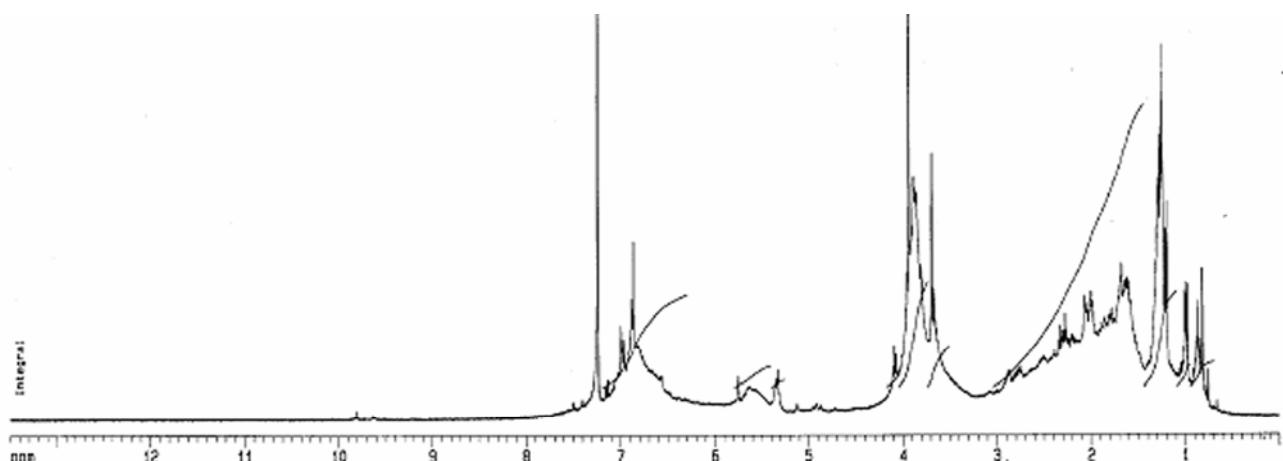


Fig. 2 ¹H-NMR spectrum of rice husk lignin (RHL)

Table 5. Chemical shift of ^1H NMR spectra of masson pine lignin

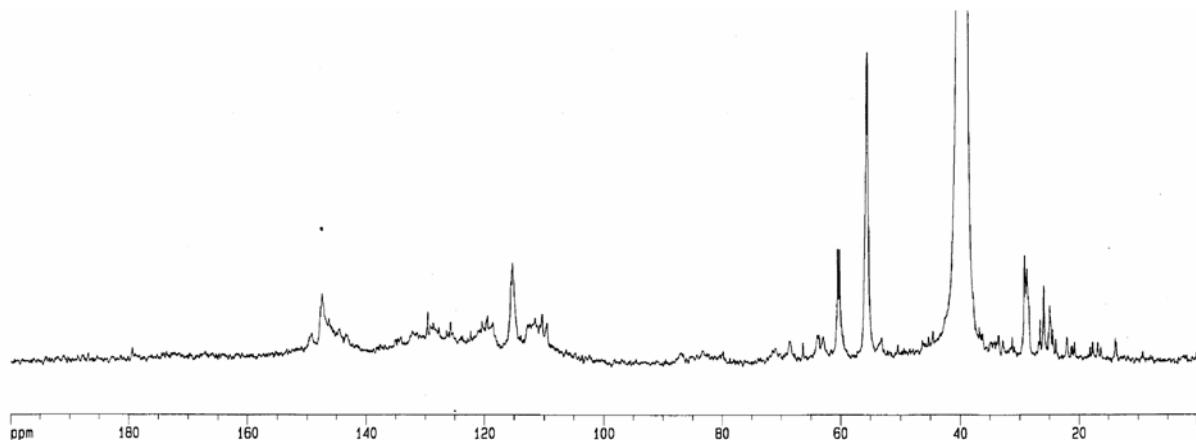
Region	Chemical shift δ (ppm)	Maximum chemical shift δ (ppm)	Types of ^1H nucleus
1	7.30	7.26	CDCl_3
	6.25–7.30		Aromatic region
	7.25–6.90	6.99	Aromatic hydrogens of guaiacyl
2	6.90–6.25	6.86	Aromatic hydrogens of syringyl
	5.20–6.25		Benzyllic Region
	6.25–5.75	5.77	Hydrogens on C- α of β -O-4 and β -1 substructures
3	5.75–5.20	5.32	Hydrogens on β -5 and α -O-4 substructures
	2.50–5.20		Methoxyl and major aliphatic region
	5.20–4.50	5.11	Hydrogens on C- β of β -O-4 substructures
4	4.50–3.95	4.09	α -Hydrogens on β - β
	3.95–3.55	3.93	Methoxyl hydrogens in aromatic moieties
	3.55–2.50	3.69	Methoxyl hydrogens in aliphatic
5	2.50–3.55	2.86	Hydrogens on C- β of β -1 and β - β substructures
	2.50–1.60	1.67	Hydrogens of acetyl region
	1.60–0.75		Nonoxygenated aliphatic region
6	1.10–1.60	1.26	Hydrogens on $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$ and $-(\text{CH}_2)_2-\text{CH}-$
	0.75–1.10	0.81	Hydrogens on $-\text{CH}_3$

 ^{13}C -NMR analysis

The ^{13}C -NMR spectra of RHL were given in Fig. 3. The signals of aromatic part of the lignin were observed in the region between 105 and 160 ppm (Sun 2002; John Wiley & Sons 1987). The carbonate units gave very weak signals above 160 ppm. The guaiacyl units gave signals at 147.5 (C-4 in etherified guaiacyl units), 144.6 (C-4 in non-etherified guaiacyl units, data not shown), 132.4 (C-1 in non-etherified guaiacyl units), 119.8 (C-6 in guaiacyl units), 115.2 (C-5 in guaiacyl units), and 111.3 ppm (C-2 in guaiacyl units). The syringyl residues were identified by signals at 152.5 (C-3/C-5 in syringyl units), 147.5 (C-3/C-5 in non-etherified syringyl units), 132.4 (C-1 in non-etherified syringyl units), and 104.2 ppm (C-2/C-6 in syringyl units). The signals at 144.6 (C-a in esterified pcoumaric acid), 130.2 (C-2/C-6 in esterified pcoumaric acid), 125.7 (C-1 in esterified pcoumaric acid), and 115.2 ppm (C-3/C-5 in esterified

p-coumaric acid) related to the esterified p-coumaric acid. Ethoxyfied ferulic acid gave signals at 166.4 ppm (C- γ in etherified ferulic acid).

Without any ambiguity, it could be revealed that p-coumaric acid was linked to lignin by ester bonds, whereas ferulic acid was linked to lignin by both ether and ester bonds, which corresponded to our previous studies on hydroxycinnamic acids in RHL. The common carbon–carbon linkages, such as β - β (C- γ in β - β units, 71.0 ppm), was also present. A very strong signal at 55.6 ppm was assigned to the OCH_3 groups in syringyl and guaiacyl units. The signals for the γ -methyl, α , β -methylene groups in n-propyl side chains of the lignin fraction appeared in the spectrum between 33.6 ppm. These findings showed that, in the samples of RHL, guaiacyl units were predominant. The above results showed that RHL was linked with guaiacyl, syringyl and p-hydroxybenzoate type.

**Fig. 3** ^{13}C -nmr spectrum of rice husk lignin (RHL)

Conclusions

Lignin can be easily separated from rice husk by HBS pulping process using 1,4-butanediol as the solvent. Their chemical weight-average molecular weights was 1939 g·mol⁻¹, and the residual polysaccharide contents was 5.12%. The ash content of RHL, only 1.5%, was lower than the lignin sulfonate.

The ¹H-NMR spectra of RHL showed the relative intensity ratio, aliphatic over aromatic methoxyl groups, situated at 3.5–3.8 and 3.8–4.0 ppm, respectively. The results from ¹³C-NMR spectra showed that β-O-4 bond and β-5 carbon–carbon linkage were found to be the major linkages between RHL units.

RHL separated by HBS method maintains the basic structure from the natural lignin. HBS method is a pulping process of rice husk with saving energy, saving resources and non-pollution. It may have potential applications to material science and engineering.

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